THERMAL STRAIN MEASUREMENTS IN EPITAXIAL $CoSi_2$/Si BY DOUBLE CRYSTAL X-RAY DIFFRACTION

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ABSTRACT

The perpendicular x-ray strain of epitaxial $CoSi_2$ films grown on Si(111) substrates at $\sim 600^oC$ by MBE was measured at various temperatures. Within experimental error margins, the strain decreases linearly with rising temperature at a rate of $(1.3\pm0.1)\times10^{-5}/^oC$ from room temperature up to 600^oC. Over that temperature range and the duration of a complete measurement ($\sim .5h$ to $\sim 2h$), these strain values remain reversible. At 593^oC, the x-ray strain is -0.85%, which is about the strain that a stress-free $CoSi_2$ film on Si(111) would have at that temperature. This results show that the stress in the epitaxial $CoSi_2$ film is fully relaxed at the growth temperature. Strains below the growth temperature are induced in the film by the difference in the linear coefficient of thermal expansion of $CoSi_2$ and Si. They were calculated by assuming that the density of misfit dislocations formed at the growth temperature remains constant. The slope of the strain-temperature dependence obtained that way agrees with the measured slope if the unknown Possion ratio of $CoSi_2$ is assumed to be $\nu_{CoSi_2} = 0.35$. A film stress of ~ 0.8 GPa at room temperature was calculated using the above value for the Possion ratio, 130 GPa for the Young modulus, and the measured x-ray strain.

INTRODUCTION

The successful growth of an epitaxial $CoSi_2$ film on a Si(111) substrate holds promise for the fabrication of novel devices such as tunneling structures and metal/semiconductor superlattices. Since the initial experimentation on epitaxial growth of $CoSi_2$ on Si[1], progress in understanding and controlling the growth process and the imperfections has been achieved. Many important structural and electrical properties of the $CoSi_2$ films have been characterized[2–3].

The atomic coordination of the epitaxial $CoSi_2$ film is rotated 180^o about the [111] axis with respect to the Si(111) substrate (type-B)[4]. The lattice mismatch, f, between the $CoSi_2$ and Si at room temperature is -1.23%. The critical thickness, t_{cr}, for pseudomorphic growth of $CoSi_2$ on Si(111) was reported to be $\sim 30\mathring{A}$[5]. The growth of $CoSi_2$ on porous Si(111) substrates was explored with the aim of increasing the critical thickness of the film[6]. Double crystal diffractometry shows that epitaxial $CoSi_2$ films grown on Si substrates, with surfaces offset from {111}, are misoriented, i.e., there is a tilt angle between the [111] directions of the $CoSi_2$ film and the Si substrate[7]. Strain measurements on thick films (i.e., the film thickness, $t_f > t_{cr}$) by double crystal diffractometry at room temperature show that the perpendicular x-ray strain $\epsilon^{\perp}$ of epitaxial $CoSi_2$ films has a typical value of about -1.65% over the range of film thickness t_f from 100Å to 2500Å[7,8] (Perpendicular x-ray strain is defined as $\epsilon^{\perp} = (d_f - d_s)/d_s$, where d_f and d_s are the interplanar spacings of (111) planes in the film and the substrate). This result differs from the value of $\epsilon^{\perp} = -1.23\%$ of a stress-free film at room temperature, which indicates that thick $CoSi_2$ films on Si(111) are under tensile stress at room temperature.

The lattice mismatch between bulk $CoSi_2$ and bulk Si at the growth temperature (~ 600°C) is estimated to be about -0.85% from the lattice mismatch at room temperature, $f = -1.23\%$, and thermal expansion coefficients of the two materials, $\alpha_{Si} = 2.7 \times 10^{-6}/^{o}C$ and $\alpha_{CoSi_2} = 9.4 \times 10^{-6}/^{o}C$[9]. Thermal stress can be induced in the $CoSi_2$ film when the sample is cooled down from the growth temperature to room temperature if there are no interface dislocations introduced to release the stress during the cooling.

In this paper, we present the results of perpendicular x-ray strain measurements of thick $CoSi_2$ films on Si at temperatures between room temperature and 600°C by double crystal diffractometry. This gives some insight on the stress state at the growth temperature, the plastic flow below the growth temperature, and the residual stress at room temperature of epitaxial $CoSi_2$ films grown on Si(111) substrates by MBE.

EXPERIMENTAL METHOD AND RESULTS

Single strained layers of $CoSi_2$ were grown epitaxially on Si(111) substrates by MBE. The surfaces of all substrates were offset from the (111) planes of the Si towards the $[1\bar{1}0]$ direction, with offset angles, ϕ_s, from 0° to 16°. The growth conditions have been described elsewhere[10]. The $CoSi_2$ was formed at about (600±50)°C. The film thicknesses of the samples used in this study are about 1000Å, which is more than 30 times thicker than the critical thickness of an epitaxial $CoSi_2$ film on Si(111) ($t_{cr} \sim 30\AA$). Rutherford Backscattering Spectroscopy and channeling with a 2 MeV $^4He^+$ beam were used to characterize the stochiometry and crystallinity of the epitaxial $CoSi_2$ films. The films have the stochiometry of the $CoSi_2$ phase (Co:Si≈ 1 : 2 within the 10% experimental error) and excellent crystallinity ($\chi_{min} \approx 3\%$).

X-ray rocking curves were taken with Fe K_{α_1} radiation diffracted from the (111) planes of a high quality Si(111) crystal. The sample was mounted on a heating stage in air. The sample temperature T was controlled between room temperature and 600°C. The symmetrical (111) diffraction was recorded and the perpendicular x-ray strain $\epsilon^{\perp}$ (strain perpendicular to (111)) was extracted.

The x-ray rocking curves of sample K310 measured at room temperature and 593°C are shown in Fig. 1. The perpendicular x-ray strain measured at 593°C is $\epsilon^{\perp} = (-0.85 \pm 0.01)\%$. This is the value of $\epsilon^{\perp}$ for a stress-free $CoSi_2$ film at that temperature. The conclusion therefore is that at the growth temperature, the film stress is fully relaxed. The perpendicular elastic strain at room temperature, $e^{\perp} = \epsilon^{\perp} - f$, calculated from the measured perpendicular x-ray strain $\epsilon^{\perp} = (-1.66 \pm 0.01)\%$ and the lattice mismatch $f = -1.23\%$ at room temperature is -0.43%. This strain is induced by the different thermal contraction of the film and the substrate, and the epitaxial constraint.

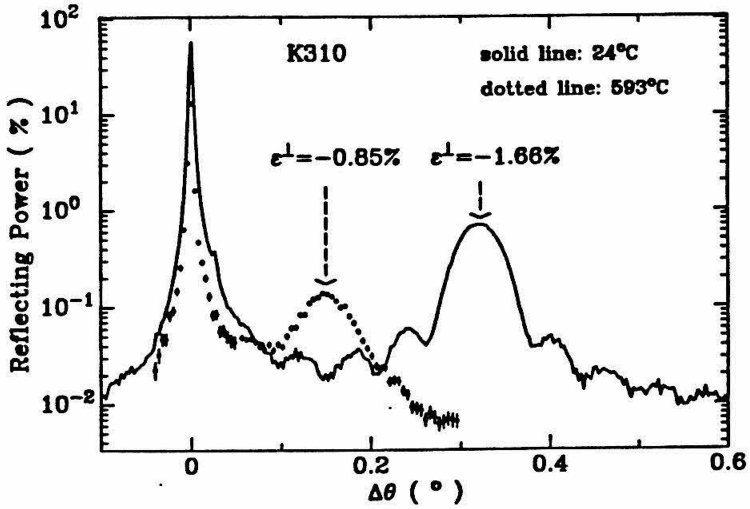

Fig. 1 *Fe* $K_{\alpha 1}$ x-ray rocking curves from the symmetrical (111) diffraction planes. The solid curve is for the measurement taken at room temperature in air. The dotted line is for the measurement taken at 593°C.

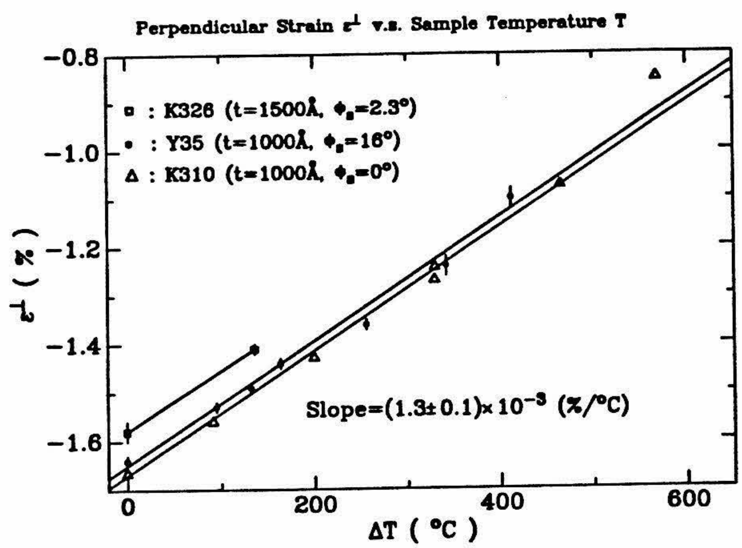

Fig. 2 Dependence of the perpendicular x-ray strain *versus* the temperature at which measurement was performed. Three sets of data are for three different samples. The slopes are same for all samples.

The results of the perpendicular x-ray strain measurements at elevated temperatures are shown in Fig. 2. There are three sets of experimental data corresponding to three different samples which have slightly different perpendicular x-ray strains at room temperature. The variations of the strain values measured at room temperature are probably due to the variations of the growth temperature. The slopes of the three curves are the same, $(1.3 \pm 0.1) \times 10^{-5}/^{o}C$, which is larger than the difference of the bulk thermal expansion coefficients between $CoSi_2$ and Si at room temperature, $(\alpha_{CoSi_2} - \alpha_{Si}) = 6.7 \times 10^{-6}/^{o}C$. This fact can be explained by assuming that the lateral change of the $CoSi_2$ lattice is constrained to be same as that of the Si substrate. The perpendicular change of the $CoSi_2$ lattice is therefore larger than that of a stress free $CoSi_2$ film due to the Possion effect. If one assumes that the misfit dislocations are locked in below the growth temperature, meaning that their numbers and positions are fixed after the growth of the film, the slope of the perpendicular x-ray strain $\epsilon^{\perp}$ versus temperature T is then given by

$$\frac{\delta\epsilon^{\perp}}{\delta T} = \left(\frac{1+\nu_{CoSi_2}}{1-\nu_{CoSi_2}}\right)\cdot(\alpha_{CoSi_2} - \alpha_{Si}),$$

where ν_{CoSi_2} is the Possion ratio of $CoSi_2$. We were unable to find its value in the literature. But if we assume that $\nu_{CoSi_2} = 0.35$ and use the value of (α_{CoSi_2}-α_{Si}) at room temperature, we obtain a slope of $1.4 \times 10^{-5}/^{o}C$, which is within 10% of the measured value (see Fig. 2). This agreement indicates that the misfit dislocation density remains unchanged in the temperature range and durations of this experiment. A direct proof of this assertion is in fact contained in the additional observation that thermal cycling of a sample does not create a hysterisis in $\epsilon^{\perp}(T)$ of Fig. 2, even for temperature up to 600°C for 2-4 hours.

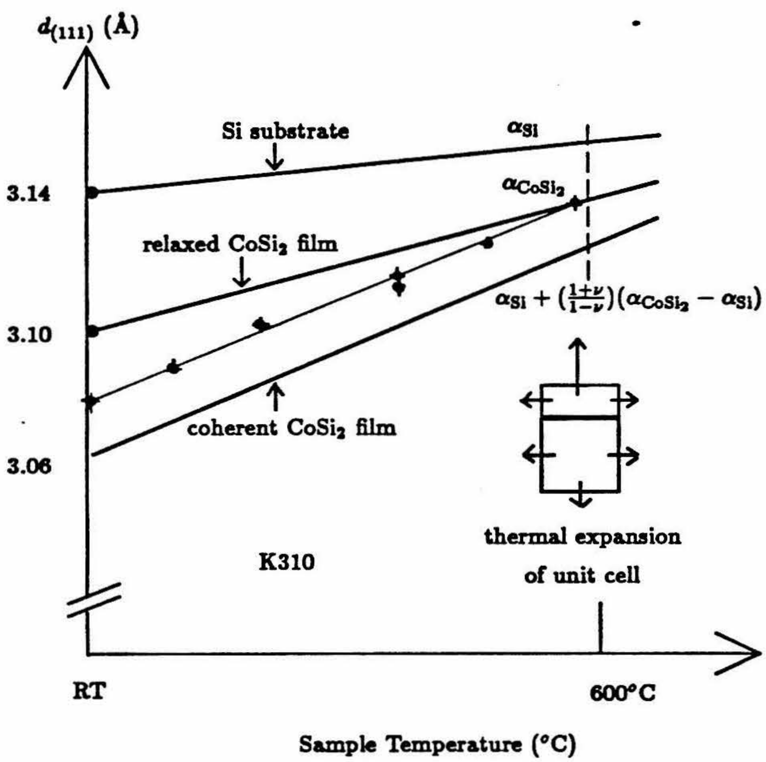

Fig. 3 Schmatic plot of the lattice constants of $CoSi_2$ and Si *versus* temperature. The experimental curve meets the curve for the bulk thermal expansion of $CoSi_2$ at the growth temperature, indicating that the $CoSi_2$ film is relaxed on Si(111) at the growth temperature. The slope of the experimental curve is parallel to the curve for the coherent $CoSi_2$ film on Si, indicating no plastic flow below the growth temperature.

DISCUSSION

In Fig. 3, the results of the strain measurements are translated into a picture that shows the lattice constants as a function of temperature. It is consistent within the experimental errors and the uncertanties in the knowledge of some parameters (such as the Possion ratio and the bulk thermal expansion coefficients of $CoSi_2$ from room temperature to 600°C) to conclude that our thick epitaxial $CoSi_2$ films ($t_f > t_{cr}$) grown on

Si(111) substrates are free of stress at the growth temperature. At that temperature, the lattice mismatch of $\sim -0.85\%$ is accomodated by misfit dislocations. When the samples are cooled to room temperature, these misfit dislocations are essentially immobile and no additional misfit dislocations are generated. As a result, thermal strains are induced in the $CoSi_2$ films by the differential thermal contraction of the film and the substrate. The $CoSi_2$ films are under tension below the growth temperature. The thermal stresses in the $CoSi_2$ films at room temperature can be calculated from the measured perpendicular strain $\epsilon^{\perp}$ at room temperature,

$$\sigma \approx -\frac{E_{\mathrm{CoSi_2}}}{2\nu_{\mathrm{CoSi_2}}} \cdot (\epsilon^{\perp} - f),$$

where $E_{\mathrm{CoSi_2}}$ is the Young modulus of $CoSi_2$. For example, using the measured x-ray strain of the sample K310 at room temperature, $\epsilon^{\perp} = -1.66\%$, and assuming the elastic constants of $CoSi_2$, $E_{\mathrm{CoSi_2}} = 130$ GPa[11] and $\nu_{\mathrm{CoSi_2}} = 0.35$, we obtain the tensile stress at room temperature in the $CoSi_2$ film, $\sigma = 0.8$ GPa. We can generalize this result to calculate the thermal stress in the $CoSi_2$ film at any temperature T below the growth temperature T_g,

$$\sigma(T) = -\frac{E_{\mathrm{CoSi_2}}}{(1-\nu_{\mathrm{CoSi_2}})} \cdot (\alpha_{\mathrm{CoSi_2}} - \alpha_{\mathrm{Si}}) \cdot (T - T_g).$$

From the experimental results and the previous discussion, we know that the above formula for the thermal stress is valid for temperature from 600°C to as low as room temperature, and for tensile stress as large as 0.8 GPa. This stress is not large enough for misfit dislocation generation or multiplication.

CONCLUSION

In summary, we have measured the perpendicular x-ray strain in $CoSi_2$ films *in situ* from room temperature to 600°C. The x-ray strain value of -0.85% measured at 600°C suggests that the thick ($t_f > t_{cr}$) epitaxial $CoSi_2$ films are relaxed on Si(111) substrates at the growth temperature. The slope of the perpendicular strain versus temperature below the growth temperature is larger than the difference of bulk thermal expansion coefficient between $CoSi_2$ and Si. This result is consistent with the model that there is no plastic flow below the growth temperature. Therefore, we conclude that the strain in the $CoSi_2$ film measured at temperatures below the growth temperature is induced by differential thermal contraction of $CoSi_2$ and Si under an epitaxial constraint. The perpendicular x-ray strain of about -1.65% measured at room temerature for thick samples ($t_f > t_{cr}$) with thickness from 100Å to 2500Å can be predicted from the elastic constants of $CoSi_2$, the bulk thermal expansion coefficients of $CoSi_2$ and Si, and the growth temperature.

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